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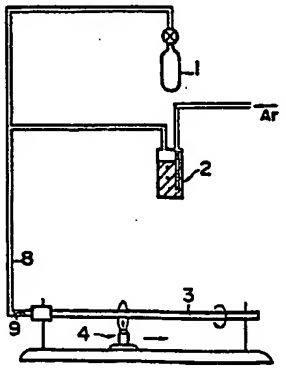
(54) Infrared optical fiber.

(57) Solid or hollow infrared optical fiber of high stability and small light transmission loss is produced from halides and/or hydrides of elements constituting calcogenide glass as starting materials by MCVD process with less chance for contamination with impurities and with unnecessity for melting for a prolonged time for homogenization.

FIG. 1



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INFRARED OPTICAL FIBER

BACKGROUND OF THE INVENTION

The present invention relates to a process for producing optical fiber capable of transmitting infrared beam.

Heretofore, optical fiber is produced from materials of silicate glass, but the materials of silicate glass have such a disadvantage that they transmit only light beams of up to wavelength of about 2 μm and absorb substantially all other beams of longer wavelength by absorption due to lattice vibration. Thus, beams of wavelength of 10.6 μm from a CO_2 laser for use, for example, in laser surgery and laser welding, etc. cannot be transmitted through the fiber of silicate glass. Accordingly, search has been so far made for materials capable of transmitting beams of wavelength from about 2 μm to about 20 μm, and as a result calcogenide glass has been regarded as a promising material for the said range of wavelengths. For example, "Infrared Physics, 1965, Vol. 5 p.p. 69 - 80" discloses infrared optical fiber of As-S glass. The conventional optical fiber of calcogenide glass is produced from powder of such metal as As, S, Ge, P, etc., or calcogen as a starting material by melting for a prolonged time. Thus, the conventional process has such a disadvantage that impurities contained in the starting

material powder of metal or calcogen are transferred into product glass, thereby increasing light transmission loss. Furthermore, the conventional process has more chance of contamination by impurities during the melting, and also requires substantial time for melting and homogenizing the powder of metal or calcogen.

The optical fiber is in such a structure that the core is made from a material of higher refractive index than that for the clad surrounding the core to utilize total reflection at the interface between the core and the clad to transmit beams. However, when a beam of a high output level, for example, 100 W, such as CO_2 laser beam is transmitted therethrough, the core material itself reaches such a high temperature as 100° - $400^{\circ}C$ due to the absorption of beams by the core material. Thus, there appear such phenomena that the core material undergoes thermal breakage or deterioration of mechanical strength. Furthermore, considerable heat generation takes place particularly at the end face of optical fiber, for example, due to fine dirts thereon or due to fine irregularity thereon, and special care is taken for its protection. Consequently, there has been a restriction to the power level of input beams.

On the other hand, MCVD process is well known as one of the conventional processes for producing optical fiber of silicate glass. According to the MCVD process, a glass film serving as a clad and a

core, or a glass film serving as a core is deposited onto an inner wall of a glass tube of quartz, etc. by the so-called CVD process utilizing chemical vapor reaction, then the glass tube is heated, thereby collapsing the hollow part and forming a rod-like optical fiber preform, and the preform is drawn with heating, thereby forming optical fiber, as disclosed in so many publications, for example, US Patent No. 4,203,743; Japanese Laid-open Patent Application No. 29953/76, etc.

The following references are cited to show the state of art; i) Infrared Physics, 1964, Vol. 4 p.p. 213 - 221, ii) Infrared physics, 1965, Vol. 5, p.p. 69 - 80, iii) US Patent No. 4,203,743, iv) Japanese Laid-open Patent Application No. 29953/76, and v) The Bell System Technical Journal, 1964, Vol. 43, p.p. 1783 - 1809.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for producing infrared optical fiber with low transmission loss, where the said problems in producing infrared optical fiber from calcogenide glass, that is, the problems of contamination of impurities and melting for a prolonged time have been solved.

Another object of the present invention is to provide a process for readily producing infrared

optical fiber where the said problem of heat generation has been solved.

The foregoing objects can be attained according to the present process for producing infrared optical fiber, which comprises i) a step of introducing into a glass tube a gas containing a halide and/or a hydride of elements constituting calcogenide glass as starting material, that is, a halide and a hydride of metal, particularly at least one element selected from the group consisting of Si, Ge, As, P and Sb, and a halide or a hydride of at least one calcogen element selected from the group consisting of S, Se and Te, and heating the glass tube, thereby depositing the calcogenide glass, that is, a compound of said metal, etc. and said calcogen element, onto the inside wall of the glass tube, and ii) a step of heating and drawing the resulting glass tube into fiber. In the step ii), the glass tube is heated at a high temperature to collapse the tube, and then drawn at a much higher temperature, whereby solid optical fiber can be obtained. Hollow optical fiber can be also obtained by heating and drawing the glass tube in a hollow state without collapsing, and dry air or infrared transmission liquid can be filled into the hollow fiber. In the case of solid fiber, the glass tube can be heated and drawn as such.

According to the present process, infrared optical fiber of high performance can be produced

without the problems, that is, without any fear of contamination of impurities and any necessity for melting for a prolonged time.

It is essential in the present process to use a halide or a hydride of the metal, etc. or calcogen element as a starting material in place of the powder of the metal, etc. or calcogen element as in the conventional process.

Furthermore, according to the present process, glass breakage due to heat generation, which has been a bottleneck in the prior art, can be avoided by using hollow fiber, and infrared optical fiber capable of transmitting a high energy level beam can be produced thereby. This is based on transmission of HE_{11} mode in a hollow waveguide of hollow optical fiber.

Optical fiber of high infrared transmittance can be obtained by making the clad from calcognide glass of high refractive index and high infrared transmittance while using air as the core. A large number of pseudo-transmitted modes (leaky modes) can be transmitted through such hollow fiber. Different from the conventional optical fiber with core of high refractive index, the pseudo-transmitted modes are waves transmitted while producing transmission loss, among which the lowest order mode (HE_{11} mode) has the least transmission loss.

According to "The Bell System Technical Journal, 1964, Vol. 43, p.p. 1783 - 1807", the

transmission loss α of HE_{11} mode is given by the following formula:

$$\alpha = \left(\frac{2.405}{2\pi}\right)^2 \frac{\lambda^2}{a^3} \cdot \frac{\frac{1}{2}(n^2+1)}{\sqrt{n^2-1}} \quad \cdots\cdots \quad (1)$$

where n represents a refractive index of glass, λ wavelength of light and a a radius of hollow part. When $n = \sqrt{3}$ in formula (1), α takes the minimum value, i.e. $\alpha = 1.8\ \lambda^2/a^3$(dB). The refractive index of calcogenide glass is usually n = 25, where the transmission loss is $2.01\ \lambda^2/a^3$(dB). When the wavelength of light is 10.6 μm and a = 2 mm, the transmission loss will be 0.028 dB/m, which is small enough, as compared with the ordinary glass and crystal, and such optical fiber can be used satisfactorily as a transmission path for high energy level beams.

Another feature of the hollow fiber produced according to the present process is use of calcogenide glass of low transmisstion loss as a clad. Substantially all of the energy of the beams transmitted through the fiber passes through the hollow part, and thus the electromagnetic field passing through the clad is small even with a high incident power, and even if the clad has transmission loss of 1 dB/m, the temperature increase of the glass by absorption is small.

The said step i) can follow the well known MCVD process except for the starting material. When solid fiber is produced, the said step ii) can also

follow the well known MCVD process. When hollow optical fiber is produced, the glass tube from the step i) is drawn at such a heating temperature and in such a drawing ratio not to cause collapsing of the glass tube while keeping the glass tube in a hollow state. The necessary heating temperature and the drawing ratio can be determined by simple preliminary test.

Any material can be used for the glass tube, so long as it can be drawn at a high temperature together with the deposited calcogenide glass. Usually, quartz glass, Pyrex glass, lead glass, etc. are used. When solid fiber is produced, collapsed optical fiber preform with the said glass tube as a crust can be drawn as such, but when the crust is removed from the preform by guiding or chemical etching and then the preform freed from the crust is drawn, infrared optical fiber consisting only of calcogenide glass can be obtained. In the latter case, any material can be used for the glass tube, so long as it can be collapsed at a high temperature together with the deposited calcogenide glass.

When the starting material is in a gaseous state at room temperature in the said step i), it can be directly introduced into the glass tube, but when it is in a liquid state at room temperature, it is bubbled with an inert gas such as Ar, etc., and the generated vapor is introduced into the glass tube

together with the inert gas as a carrier gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing an apparatus for depositing calcogenide glass onto the inside wall of a glass tube by local heating of the glass tube according to one embodiment of the present invention.

Fig. 2 is a schematic diagram showing an apparatus for depositing calcogenide glass onto the inside wall of a glass tube by uniform heating of the glass tube.

Fig. 3 is a schematic diagram showing an apparatus for depositing calcogenide glass onto the inside wall of a glass tube whose heating part for reaction is separated from a deposition part.

Fig. 4 is a cross-sectional view of hollow fiber having a calcogenide glass layer on the inside wall of a glass tube.

Fig. 5 is a schematic view showing an apparatus for depositing calcogenide glass onto the inside wall of a glass tube by local heating of the glass tube according to another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in detail below by way of a case of producing As-S glass fiber, referring to the drawings.

In the production of As-S fiber glass, $AsCl_3$ and H_2S are used as starting materials. $AsCl_3$ is in a liquid state at room temperature, and thus a bubbler 2 is used as shown in Fig. 1, $AsCl_3$ is placed in the bubbler 2 and bubbled with Ar. $AsCl_3$ is introduced into a glass tube 3 through a gas line 8 together with Ar. On the other hand, H_2S is in a gaseous state at room temperature, and is led to the glass tube 3 through the gas line 8 from a cylinder 1 directly. That is, a raw material gas of $AsCl_3$, H_2S and Ar in mixture is led to the glass tube 3 through the gas line 8 in the arrow direction 9.

Then, the raw material gas is heated in the glass tube 3 and thermally decomposed to deposit As-S onto the inside wall of the glass tube 3. Heating can be carried out by an electric furnace or a gas burner. In Fig. 2 heating is carried out by a gas burner 4.

In Fig. 1, the glass tube 3 is locally heated by the gas burner 4, and the gas burner 4 is moved in the longitudinal direction of the tube at the same time to obtain a deposit film of uniform composition and uniform thickness in the longitudinal direction. It is also possible to rotate the tube to form a uniform deposit in the circumferential direction.

Such local heating is however one example, and the glass tube 3 can be heated to the full length of glass tube by an electric furnace 5, as shown in Fig. 2, or a heating part 6 for chemical vapor reaction

of the raw material gas can be separated from a deposition part 7 usually at a lower temperature than that of the heating part, as shown in Fig. 3. Anyway, the raw material gas mixture is introduced into the glass tube 3 through the gas line 8 in the arrow direction 9.

The glass tube onto whose inside wall As-S glass is deposited in the foregoing manner is heated and drawn into fiber. In the production of solid fiber, usually the As-S glass-deposited glass tube is heated and collapsed to form optical fiber preform, and then the preform is drawn at a much higher temperature, whereas in the production of hollow fiber, the As-S glass-deposited glass tube is directly heated and drawn so that no collapsing can occur. In the production of solid fiber, the As-S glass-deposited glass tube can be also directly heated and drawn without forming the preform.

First of all, the production of solid fiber will be described in detail below:

The As-S glass-deposited glass tube is further heated for collapsing. Heating for the collapsing can be local heating by a burner, where the heating part is moved in the longidinal direction of the glass tube. In that case, heating can be uniformly carried out in the circumferential direction of the glass tube by rotating the glass tube. Collapsing can proceed under the inside pressure of the glass tube

equal or a little inferror to the atmosphere, but the As-S glass is liable to vaporize, the tube inside is made vacuum and the ends of the tube are sealed before the collapsing is carried out. The thus prepared solid rod is called "preform".

Then, the preform is drawn into fiber in the same manner as in the conventional drawing of a preform of quartz glass fiber. In that case, the resulting fiber has oxide glass, which is the constituent of the glass tube 3, as a crust. By removing the oxide glass from the preform by guiding or chemical etching beforehand, optical fiber consisting only of As-S glass can be obtained.

The foregoing process is directed to the production of As-S glass fiber having a uniform composition in the radial direction. Clad-type fiber of double layer structure consisting of a core of high refractive index and a clad of low refractive index, or graded index-type fiber whose refractive index is gradually increased from the peripheral part toward the center can be produced by changing the composition in the radial direction in the following manner.

The composition can be changed in the radial direction by reciprocating the burner of heating the glass tube while moving in the longitudinal direction of the glass tube several times in the longitudinal direction, while changing the composition of raw material gas to the glass tube at every reciprocation

or at a specific reciprocation. The composition of raw material gas can be changed by changing a mixing ratio of $AsCl_3$ to H_2S, or by adding other additive such as $GeCl_4$ thereto to change the concentration.

Production of hollow fiber will be described in detail below.

The As-S glass-deposited glass tube is drawn in the same manner as in the conventional drawing of quartz glass fiber. In that case, heating temperature and drawing ratio must be so selected as not to collapse the glass tube. The thus produced optical fiber is hollow fiber having As-S glass on the inside wall of the glass fiber, as shown in Fig. 4, where numeral 10 is an air core, numeral 11 a calcogenide layer, and numeral 12 a drawn glass tube.

In the foregoing, only the case of using $AsCl_3$ and H_2S as the starting materials has been described for both solid fiber and hollow fiber. Besides the foregoing starting materials, AsH_3, $AsBr_3$, AsI_3, etc. can be also used for As, and S_2Cl_2, SCl_2, etc. for S.

In the foregoing, description has been made only of the fiber of As-S glass. The present process is however not limited only to the As-S glass fiber, but also to other calcogenide glass fiber. Other calcogenide glass than the As-S glass includes: (1) Ge-Sb-S; (2) Ge-Sb-Se; (3) Ge-As-S; (4) Ge-As-Se; (5) Ge-S-P; (6) Ge-Se-P, etc. Typical composition

of calcogenide glass for use in the present process is combinations of at least one of Si, Ge, As, P and Sb with at least one of S, Se, and Te. Besides the foregoing elements, Cl, Br or I can be added thereto. The present process is applicable not only to the compositions as defined above, but also to calcogenide glass of other compositions as defined above.

As described above, the present process has such advantages as less chances for contamination of a product with impurities and unnecessity for melting for a prolonged period for homogenizing the composition, and is very effective for production of optical fiber with low transmission loss.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

$GeCl_4$ and $SbCl_5$ were used as compounds of metal, etc, and Se_2Cl_2 as a calcogen compound as starting materials, and the apparatus shown in Fig. 5 was used. $GeCl_4$ was placed in a bubbler 2 and bubbled with Ar. $SbCl_5$ was placed in a bubbler 2' and bubbled with Ar. Se_2Cl_2 was placed in a bubbler 2" and bubbled with Ar. A raw material gas of $GeCl_4$, $SbCl_5$ and Se_2Cl_2 carried by carrier Ar gas was introduced into a glass tube 3 of lead glass (outer diameter: 14 mm, inner diameter: 12 mm) through a gas line 8 in the arrow direction 9. $GeCl_4$, $SbCl_5$ and Se_2Cl_2 were all in a liquid state at room temperature and were bubbled at

20°C. The composition of the raw material gas was controlled by bubbling of Ar to 43 mg/s of $GeCl_4$, 30 mg/s of $SbCl_5$ and 137 mg/s of Se_2Cl_2.

Chemical vapor reaction was carried out by using an oxygen-hydrogen burner 4 reciprocating at a rate of 0.2 cm/s in the logitudinal direction of the glass tube 3, while rotating the glass tube 3 at 40 rpm. Heating temperature was found to be 600°C by an optical pyrometer. After the heating oxygen-hydrogen burner 4 was reciprocated in the longitudinal direction of the glass tube 3 by 50 repetitions, the glass tube was fused at about 800°C to collapse the glass tube into a preform.

Then, the thus obtained preform was drawn at 800°C into optical fiber with a Ge-Sb-Se glass part having an outer diameter of 50 μm and a crust glass part having an outer diameter of 150 μm.

The glass tube consisted of lead glass, and the calcogenide glass consisted of 28 mol.%Ge - 12 mol.%Sb - 60 mol.%Se. The thus obtained optical fiber had light transmission loss of 0.1 dB/m at the wavelength of 10.6 μm, and thus the infrared optical fiber with considerably smaller light transmission loss than that of the conventional optical fiber was obtained.

Example 2

A Ge-Sb-Se glass film was deposited on the

inside wall of a glass tube in the same manner as in Example 1, except that the glass tube of lead glass having an outer diameter of 14 mm and an inner diameter of 13 mm was used and the heating oxygen-hydrogen burner 4 was reciprocated in the longitudinal direction of the glass tube by 100 repetitions.

The calcogenide glass film-deposited glass tube was heated in an electric furnace at 800°C and drawn into hollow glass fiber. The hollow glass fiber had an outer diameter of 4 mm, an inner diameter of 1.5 mm and a calcogenide glass film thickness of 300 μm.

The lead glass of the glass tube consisted of 57 mol.%SiO_2 - 12 mol.%Na_2O + K_2O - 30 mol.%PbO, and the deposited calcogenide glass had the same composition as in Example 1.

The thus obtained hollow infrared optical fiber had light transmission loss of 0.7 dB/m at the wavelength of 10.6 μm, and had a temperature elevation by only a few tens of degree °C even with an incidental CO_2 laser beam of 50 W, and thus the infrared optical fiber with a high stability and small light transmission loss, as compared with those of the conventional optical fiber was obtained.

Example 3

In the foregoing Example 1, solid optical fiber having a uniform composition in the radial

direction was produced, whereas in the present Example 3, glass fiber having changing composition in the radial direction was produced by using the same apparatus as shown in Fig. 5 and used in Example 1.

In the present Example 3, 43 mg/s of $GeCl_4$, 60 mg/s of $SbCl_5$ and 137 mg/s of Se_2Cl_2 as the starting materials were used up to 25th repetition of reciprocal movement of the burner in the longitudinal direction of the glass tube, and 43 mg/s of $GeCl_4$, 30 mg/s of $SbCl_5$ and 137 mg/s of Se_2Cl_2 were used from 26th repetition to 50th repetition. Other conditions were the same as in Example 1.

The thus obtained preform was drawn into fiber.

An optical fiber having light transmission loss of 0.01 dB/m at the wavelength of 10.6 μm was obtained.

It seems that considerably smaller light transmission loss in Example 3 than in Example 1 is due to the fact that the present fiber consisted of a core and a clad and had no substantial influence by the surrounding glass tube.

The thus obtained clad-type fiber had a core diameter of 50 μm, a clad thickness of 50 μm and total diameter of 150 μm, and the core consisted of 28 mol.%Ge - 12 mol.%Sb - 60 mol.%Se, and the clad consisted of 23.5 mol.%Ge - 12 mol.%Sb - 64.5 mol.%Se.

Obviously many modifications and variations

of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practised otherwise than as specifically described.

CLAIMS:

1. A process for producing infrared optical fiber which comprises:

i) a step of introducing a gas containing halides and/or hydrides of elements constituting calcogenide glass into a glass tube and heating the glass tube, thereby depositing onto the inside wall of the glass tube calcogenide glass resulting from chemical vapor reaction, and

ii) a step of heating the glass tube from the step i) and drawing the tube into fiber at a high temperature.

2. The process according to Claim 1, wherein the calcogenide glass is a compound of at least one element selected from the group consisting of Si, Ge, As, P and Sb, and at least one element selected from the group consisting of S, Se and Te.

3. The process according to Claim 1 or 2, wherein the step ii) comprises heating the glass tube, thereby forming a solid optical fiber preform, and drawing the preform into solid fiber at a high temperature.

4. The process according to Claim 1 or 2, wherein the step ii) comprises drawing the glass tube into hollow fiber without collapsing the glass tube.

5. The process according to Claim 3, wherein the preform is drawn into fiber at a high temperature after the crust of the preform has been removed.

FIG. 1

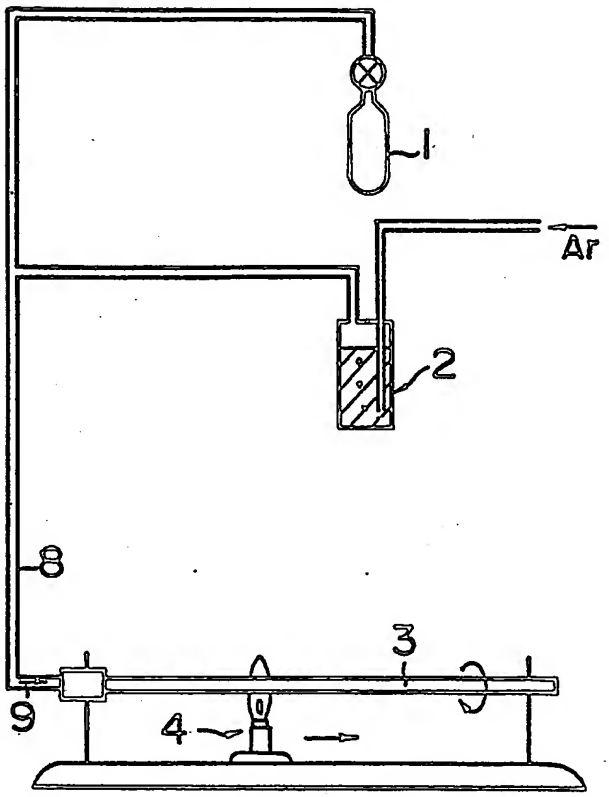


FIG. 2

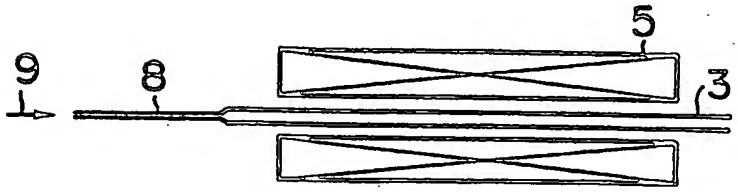


FIG. 3

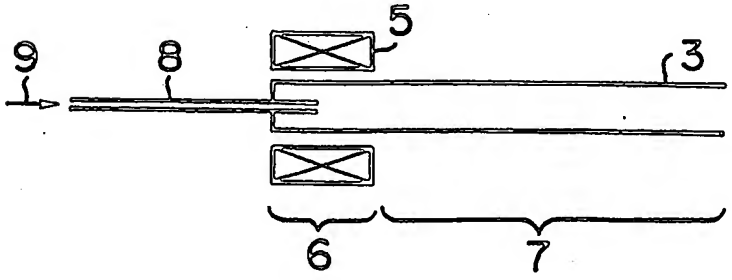


FIG. 4

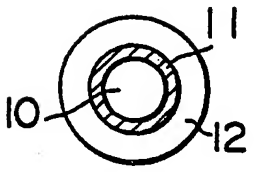
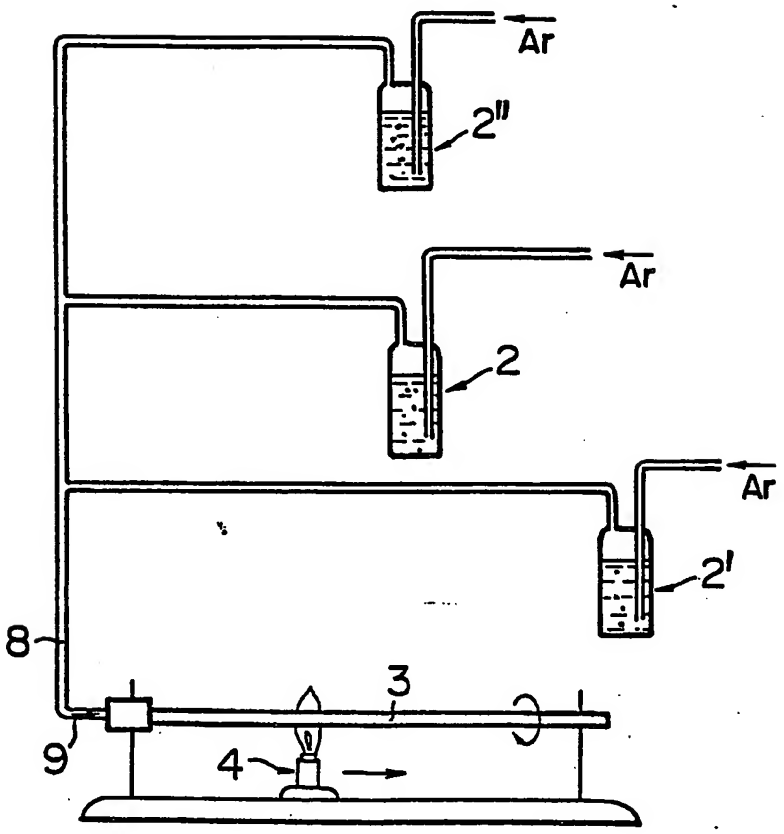


FIG. 5



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EUROPEAN SEARCH REPORT

Application number

EP 82 30 1088

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	US-A-4 188 089 (G. GLIEMER ROTH) * claims 1,2,4,6,7,12 *	1-3	G 02 B 5/172 C 03 B 37/02
A	US-A-3 980 459 (TINGYE LI) * summary; figures *	1	
A	FR-A-2 384 722 (I.S.E.C.) * claims *	1	
A	DE-B-2 546 162 (JENAER GLASWERK) * columns 3,4 *	1	
A,D	US-A-4 203 743 (T. SUGANUMA et al.) * abstract *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

G 02 B 5/172
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-06-1982	PFAHLER R.

CATEGORY OF CITED DOCUMENTS

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